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The expression in brackets on the right-hand side represents the effective quartic coefficient (a_g or a_e depending on m) for eq 71 and 72 since $Q_1^4 = \mu_1^2 x^4$. From eq 74 using first $m = 0$ and then $m = 1$ and taking the difference and rearranging, we have

$$a_{22} = \frac{\mu_2 \bar{\nu}_2^{-3/2}}{23.8202} (a_g - a_e) \quad (75)$$

This provides a good approximation for a_{22} , which would otherwise be difficult to obtain.

Conclusion

We have presented a review of the development of the vibrational Hamiltonian from fundamental principles. We have also presented the formalism for quantum-mechanical calculations necessary to arrive at a potential energy surface representing the interaction between two vibrational modes, which can to a first approximation be treated separately from the other $3N - 8$ vibrations. The theoretical treatment, which is aimed at determining a specific potential energy surface, assumes the availability of

appropriate data from vibrational spectroscopy. The determination of a two-dimensional potential energy surface is necessary for a thorough understanding of the conformational dynamics of a molecule. The general procedures presented here have been widely used in our laboratory to determine kinetic and potential energy surfaces for a variety of small ring molecules.⁹⁻¹¹

Recently, the two-dimensional potential energy surface for 3-phospholene has been reported.⁹ The techniques presented here were used extensively to arrive at a potential energy surface for this molecule. Several approximations were made using the Van Vleck transformation, and these were useful in arriving at the final potential energy surface.

The techniques presented here are most useful for studying vibrations that are separable from all other vibrations in the molecule. The expansion of the techniques to the study of vibrations in systems other than small ring molecules has not been widely investigated, but this has considerable potential.

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Clusters of Organic Molecules in a Supersonic Jet Expansion

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A wide variety of clusters were obtained in seeded supersonic conical jet expansions of organic molecules. It was shown that mixed clusters probably are formed statistically in the collisional region of the expansion, although kinetic effects cannot be excluded. The molecular fragmentation in the clusters upon mass selection using electron impact ionization is negligible, which makes the use of supersonic jet expansions under cluster forming conditions a valuable addition to standard mass spectrometry analytical techniques. The effect of the electron impact ionization on cluster fragmentation was studied.

Introduction

Clusters form aggregates which can be thought of as intermediate between the solid, the liquid, and the gas phase. A study of cluster properties may yield important information for such fields as the catalysis of chemical reactions and condensation and solvation effects, and clusters may even be used as a model for the study of surface phenomena. The properties of the clusters generated in a supersonic jet expansion can be studied by a range of optical, mass spectrometric, and electron excitation methods. In addition molecular dynamics calculations can provide us with a theoretical foundation for the experimental observations. By consequence the observation of cluster formation in a supersonic expansion¹ has opened up a whole new field of research, although only a limited amount of work in this area has been done so far.

Sievert et al.² produced small acetic acid clusters and analyzed them by electron impact (EI) mass spectrometry. They found extensive fragmentation upon ionization and a high yield of the $(M + H)^+$ peak which originates from the $(M - M)^+ \rightarrow (M + H)^+ + (M - H)$ cluster fragmentation reaction. Bernstein et al.³ studied toluene clusters in a supersonic beam and used EI and multiphoton ionization (MPI) mass spectrometry for detection and found less molecular and cluster fragmentation with the latter technique. An interesting observation was the different time

profiles in their pulsed experiments for the monomer and the higher clusters. Fung et al.⁴ generated mixtures of benzene- h_6 and benzene- d_6 clusters and analyzed the beam with MPI. They found that the excitation was mostly localized on one molecule of the cluster. Shinohara⁵ generated ammonia clusters and found more cluster formation at higher stagnation pressure and for a higher molecular weight of the carrier gas. Smalley et al.⁶ did some elegant experiments in which they generated metal atom clusters by laser evaporation, and their experiments resolved some old theoretical problems about the electronic properties of diatomics.

Finally, Stace⁷ recently showed extensive argon clustering around acetone and proposed a mechanism for their breakup upon electron ionization.

Other methods, such as secondary ion mass spectrometry⁸ and fast atom bombardment spectrometry⁹ have been used to generate

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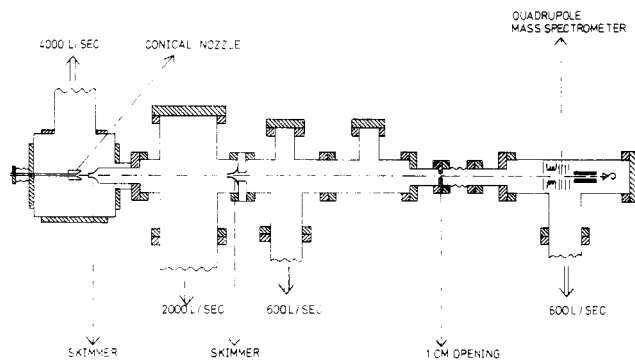


Figure 1. Molecular beam apparatus.

neutral and charged clusters. But these methods are destructive and the formed clusters frequently do not reflect the original molecular composition of the bombarded solid.

Our method of cluster generation consists of a minor modification of a supersonic nozzle expansion, in that the nozzle was made conical in shape, thus probably extending the collision region and in any case leading to a high yield of large clusters of essentially all molecules that were seeded in the He expansion.

Our purpose is to study the formation kinetics of mixed clusters of organic molecules, which may give us a very sensitive tool for probing intermolecular interactions. Another area of interest is the behavior of clusters during optical or electron beam excitation. A study of the latter is important because the initial cluster distribution may be severely disturbed by the ionization process required for mass selection. Finally, we will explore the usefulness of cluster generation for analytical applications of mass spectrometry, where the analysis of mixture is often difficult through the extensive fragmentation of the parent molecular ions.

Experimental Section

The experiments were performed on a pulsed doubly skimmed multipurpose supersonic beam instrument with facilities for optical excitation and detection of the beam constituents and equipped with a quadrupole mass spectrometer. Figure 1 gives a schematic diagram of the instrument. The gas is injected into the system by a Bosch fuel injection valve equipped with a conical headpiece with a hole of 0.2–1.0 mm and an opening angle of 30–60°. This shape increases cluster formation very considerably. The conical design also increases the beam pressure by at least 1 order of magnitude through its focusing effect. The valve operates at a frequency up to 100 Hz and has an effective opening time of 0.5 ms. Helium or argon was used as carrier gas and the backing pressure could be regulated between 0.1 and 50 bar.

The beam passes through an expansion chamber which is pumped by an Edwards 18B4A 4000 L/s Vapour Booster backed by an Edwards ES4000 single-stage rotary pump. The pressure in the expansion chamber can be maintained between 10^{-3} and 10^{-4} torr when the beam is operating. This expansion chamber is equipped with optical windows for laser excitation of the beam and a quartz fiber for detection of the resulting emission. The beam passes between 1 and 4 cm downstream from the nozzle through a conical skimmer with an opening of 1.5 mm to the second chamber. This chamber, as the next ones, is constructed from stainless steel, and all seals are made by oxygen-free high conductivity copper gasket sealed knife-edge flanges. The diameter of this second chamber is 25 cm, and it is pumped by a water baffled Edwards 250/2000 Diffstak 2000 L/s diffusion pump backed by an Edwards E2M40 double-stage rotary pump. A pressure of 10^{-6} – 10^{-7} torr can be maintained with the beam in operation. This chamber too is equipped with optical windows for laser excitation and quartz fibers for detection. At 50 cm downstream from the first skimmer the beam passes through a 1-mm-diameter conical skimmer into the third 15-cm-diameter

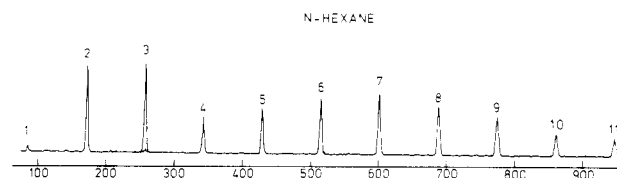


Figure 2. Cluster mass spectrum (CMS) of *n*-hexane.

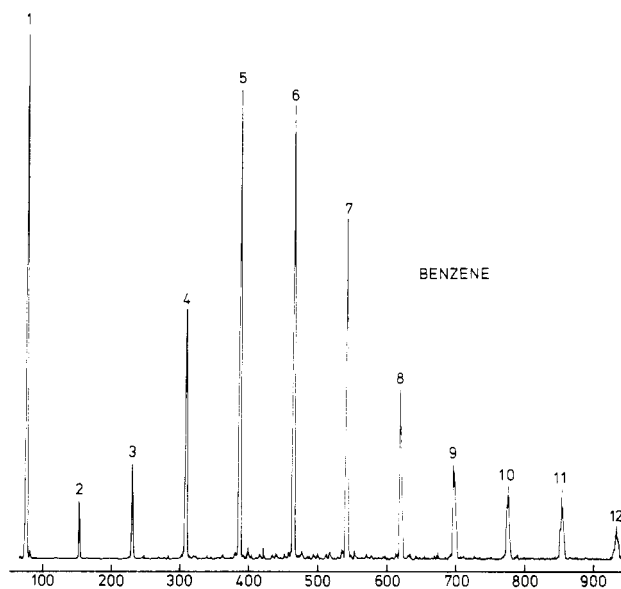


Figure 3. CMS of benzene. The first peak on the left is the monomer, then clusters 2–12.

chamber which is pumped by a liquid nitrogen trapped 600 L/s Edwards E04 diffusion pump backed by an Edwards E2MB double-stage rotary pump. This chamber can be equipped with the previously described optical excitation and detection equipment as well. A pressure of 10^{-8} torr can be maintained with the beam running. The pressure in this chamber can be regulated in order to allow for collision induced cluster fragmentation experiments. About 100 cm downstream from the second skimmer the beam passes through a 1-cm opening into the mass spectrometer chamber which is pumped by a liquid nitrogen trapped 600 L/s Edwards E04 diffusion pump backed by an Edwards EDM12 double-stage rotary pump. Under experimental conditions a pressure of 5×10^{-9} torr can be maintained in this chamber. The total flight path from the nozzle up to the mass spectrometer entrance in the last chamber amounts to 2 m.

The mass spectrometer is a quadrupole (Extranuclear) operated at ca. 1.6 MHz with a mass range of 1000 amu. The molecular beam electron impact ionizer operates with energies between 10 and 100 eV and emission currents between 1 and 50 mA. An Einzel lens focuses the ions created in the ionization region into the entrance of the mass filter. The positive ions are detected by a 14-stage venetian blind particle multiplier which can be operated in either a direct-current or a pulse counting mode. The mass spectrometer signal is time analyzed by a Parr 162 boxcar integrator and collected in an Apple II computer or directly read out on an x-y recorder.

All chemicals and gases used were of high purity grade. All gases were expanded at ambient temperature. Gas mixing was done by establishing equilibrium between the organic material and the carrier gas at ambient temperature, while the composition of the mixtures was carefully controlled by adjusting the independent gas flows with needle valves, which were monitored by calibrated flow meters.

Results and Discussion

Essentially all organic molecules introduced into the beam showed extensive cluster formation. Figures 2 and 3 show the mass spectra from 2 to 1000 amu (the limit of our instrument) for *n*-hexane and benzene. Many similar spectra were obtained

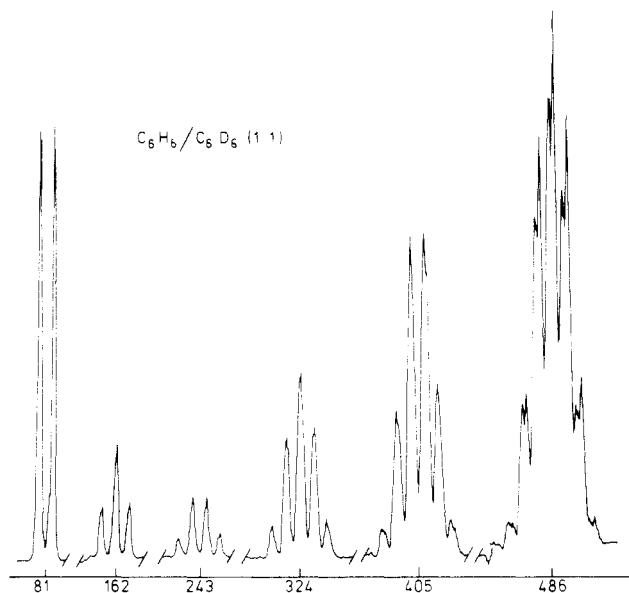


Figure 4. CMS of a 50/50 mixture of C_6H_6/C_6D_6 for the monomers and the clusters 2, 3, 4, 5, and 6.

for *n*-pentane, *n*-heptane, toluene, methanol, ethanol, and propanol, as well as for acetonitrile. We will call these clusters *neat* in contrast to the *mixed* ones, and we will discuss them further below. In all cases cluster formation up to 1000 amu was observed, and measurements of total mass above 1000 amu showed there are a considerable number of even higher clusters. Crude estimates of the cluster yield, by comparing the conventional part of the mass spectrum (below the monomolecular mass) with the cluster portion, yielded more than 90% cluster yield, depending on the settings of mass spectrometer and nozzle pressure. Except for molecules with hydrogen bonds, there appears to be no molecular fragmentation of the molecules inside a cluster upon electron impact ionization. In any case only very rarely a fragment was found attached to at most a single molecule. This lack of fragmentation is probably due to the presence of an internal "heat bath" in the clusters. The excess energy in the ionized cluster is probably easily dispersed in the degrees of freedom formed by the "phonons" of the cluster.

There does appear to be fragmentation of the clusters themselves upon ionization. In any case, the observed mass distribution is strongly affected by the energy of the electrons as it is varied between 10 and 100 eV. Since, however, nothing as yet is known about the ionization efficiencies of the clusters as a function of impact energy no quantitative conclusions can be drawn from these data.

One more observation may be worth reporting yet about the neat clusters. Normally, for aliphatic hydrocarbons, and particularly for the larger ones like *n*-heptane and *n*-octane, the so-called "parent peak" is very weak. In the cluster experiments, where it should be called the "monomer" its intensity is considerably enhanced compared to the normal fragmentation spectrum. It could be that it results from the breaking up of smaller clusters, dispersing the excess energy in the breaking of the van der Waals bond and the resulting kinetic energy of the cluster fragments.

In addition to the neat compounds we studied three classes of binary mixtures: first, mixtures of isotopically substituted compounds, second, mixtures of compounds with different intermolecular van der Waals interactions, and third, mixtures of compounds with stronger intermolecular interactions like hydrogen bridges and large dipole moments. We tried to elucidate the initial cluster distribution and its distortion by the ionization process required for mass selection.

Figure 4 shows the mass spectrum resulting from the expansion of a 50/50 mixture of benzene- h_6 and benzene- d_6 in 2-bar helium. The resulting distribution is a 1:1 binomial one which proves that the cluster formation process and the cluster fragmentation process following ionization is statistical for mixtures of very similar

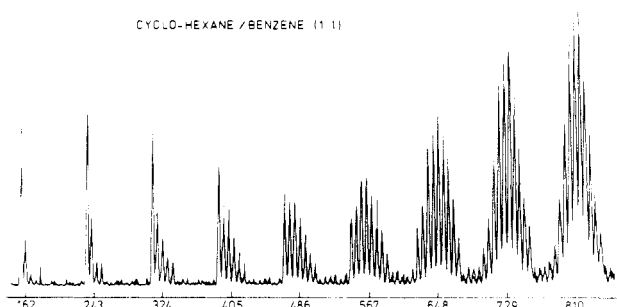


Figure 5. CMS of a 50/50 vapor mixture of benzene and cyclohexane.

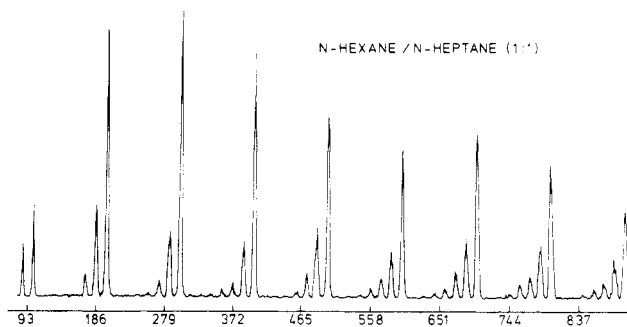


Figure 6. CMS of a 50/50 vapor mixture of *n*-hexane and *n*-heptane. The little peaks to the left of the main ones are due to the hexane-containing clusters, of which there are only very few.

molecules and is for instance not influenced by the availability of low lying C-D vibrations. The isotopic composition of the mixture can be accurately derived from the heights of the various peaks of a particular cluster size.

Cyclohexane and benzene form a binary system in which there is a larger difference in intermolecular interaction than in the previous case; i.e., the van der Waals interaction should be more attractive between the benzene molecules than between the cyclohexane ones.

Figure 5 shows the cluster mass spectrum of a 50/50 vapor mixture of benzene and cyclohexane. Clearly mixed clusters are observed, but they are all much richer in benzene than expected from a 1:1 binomial distribution of such a mixture, particularly so for the smaller clusters. This turns out to be a general observation. The compound with the weakest van der Waals bonding—as judged by the conventional ideas about the lengths of alkanes, the presence of π -electrons, etc.—always shows up as the "loser" in the mass spectrum. For instance Figure 6 shows a spectrum of a 50/50 vapor mixture of hexane and heptane, and clearly the heptane "wins". Of course, the distributions can be "forced over" by adding more of the more weakly bonded compound. For instance, Figure 7 shows a cluster mass spectrum for, again, benzene and cyclohexane, and for the clusters of 5 or 6 molecules it looks about like a 1:1 binomial distribution. In reality, however, the ratio of the partial pressures of cyclohexane to benzene was 9.

The question arises, whether this is due to a kinetic mechanism (in the nozzle), or whether it is the result of the preferential breaking up of the weaker clusters upon ionization in the mass spectrometer. At this moment no definite answer can be given, but some experiments, varying the electron energy may give some indication.

We first define the apparent mole fraction in a cluster. This is the mole fraction that can be derived from the intensities of the peaks in a particular cluster size assuming it is a binomial distribution. Except for the 3-clusters this can usually be done rather reliably. We determined the apparent mole fractions of the various clusters (except for the 3-cluster) as a function of electron impact energy. The results are given in Figure 8, where the real mole fraction in the vapor phase has also been drawn.

The electron energy has a considerable influence on the apparent cluster mole fractions and at lower energies they clearly appear to extrapolate to the real mole fraction in the vapor phase. Also,

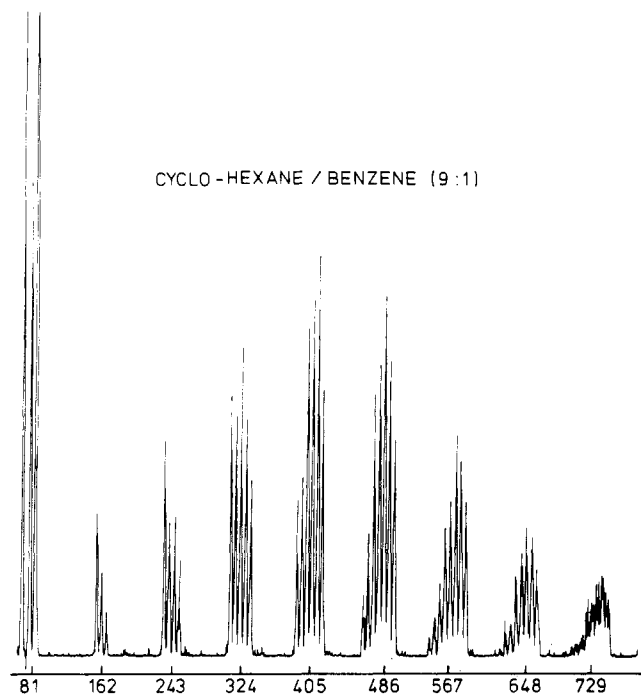


Figure 7. CMS of a 1/9 vapor mixture of benzene and cyclohexane. The clusters 5 and 6 look like a 1:1 binomial distribution.

the larger clusters appear to be much more "statistical" (i.e., obey the binomial distribution) than the smaller ones. Probably, high energy electrons (i.e., from 40 to 100 eV) deposit more energy upon ionization in the cluster than low energy electrons (20–40 eV). In any case, it is noteworthy that above 50 eV no further cluster breakup is observed, probably indicating that the amount of energy left behind after ionization is not further increased. Therefore, the ionization must cause cluster breakup, with a preference for shaking off the most weakly bonded compound.

Cluster breakup upon ionization has been observed before. In a very elegant two beam experiment Buck and Meyer¹⁰ showed that, for instance, (Ar)₃ clusters break up completely through electron ionization.

Unfortunately, the electron ionization effects on the apparent concentration prevent us from saying much about the kinetics of cluster formation. Is it statistical in nature, or is there already a preference for the more strongly bonded compound in the formation? Or, phrased in another manner, how good a "heat bath" is provided by the flowing helium? The fact, however, that at least for the larger clusters, the apparent concentration approximates the real vapor concentration appears to indicate that the kinetic effects on cluster composition are minor. Gentler

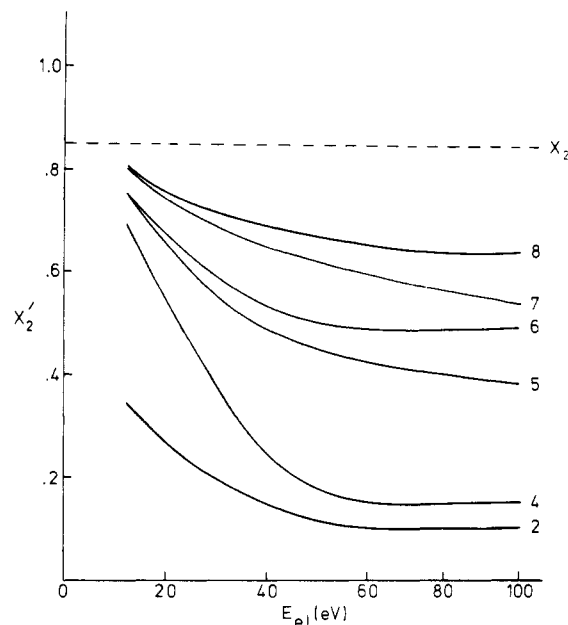


Figure 8. Apparent molar fraction (x'_2) of cyclohexane in the various clusters as a function of the electron energy. x_2 is the molar fraction in the original vapor mixture.

techniques, such as laser ionization, may establish this point more firmly.

A few words may be in order about analytical applications. Our measurements clearly show that large clusters are present in a conical nozzle expansion, much larger even than measured in our limited mass range. Also, the higher clusters appear to reflect the composition of the vapor phase rather accurately. It is conceivable, therefore, that mass spectrometers with a higher mass range and with sufficient mass resolution may be used to directly determine vapor compositions.

Conclusions

Supersonic beams produced by conical nozzles yield large molecular clusters in high yields. When studied mass spectrometrically, mixed clusters tend to break up upon ionization, shaking off the most weakly bonded compound. This effect is so subtle that it can conceivably be used to construct an "electrochemical" series for van der Waals bonding. Molecular fragmentation is almost totally absent in van der Waals clusters, probably because they offer a very good heat bath for the excess energy. It is conceivable that the largest mixed clusters may be used to determine directly vapor compositions.

Acknowledgment. We are highly indebted to Mr. W. Zevenberg for his skillful construction of the equipment.

Registry No. C₆H₆, 71-43-2; C₆D₆, 1076-43-3; *n*-hexane, 110-54-3; cyclohexane, 110-82-7; *n*-heptane, 142-82-5.

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